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Transient and quasi-stationary simulation of heat and mass transfer in Czochralski silicon crystal growth

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The formation of grown-in defects in silicon crystals is controlled by the concentration of intrinsic point defects. Under steady state conditions the type of the prevailing point defect species is linked to the ratio of pull rate and temperature gradient in the crystal at the solidification front. It has been shown that this ratio as well as computed point defect distributions are in good agreement with experimental data. In this paper we compare a coupled transient heat transfer and transient point defect transport model with quasi steady state simulations at various time steps. Both simulations show the same qualitative results, quantitative differences in temperature are less than 1 %. But already for constant pull rates the defect distributions show qualitative differences between transient and quasi steady state simulations. Therefore, for a detailed understanding how defects are related to growth conditions, the thermal history should not be neglected.

1 Introduction

Today, it is well known that the concentration of intrinsic point defects in a growing silicon crystal can be qualitatively explained as a function of the pulling rate *v* and the temperature gradient *G* at the solidification interface. At a critical ratio of $v/G = 2.23$ e-09 m^2/Ks, [1], interstitials and vacancies annihilate each other, and the crystal shows neither dislocation loops nor voids. Below that critical value, interstitials dominate, and at higher values vacancies are in excess. The *v/G* theory assumes steady state conditions during the whole growth process. For grown-in defect formations this is realized when the pull rate remains constant during the growth until the crystal has reached a temperature of approximately 1200 K. This defect formation has been extensively studied experimentally and theoretically for almost steady state growth conditions. For widely varying growth conditions it has been shown that the *v/G* criteria as well as computed point defect distributions are in good agreement with experimental data.

In this paper we solve a coupled transient heat transfer and transient point defect transport model and compare the results with quasi steady state calculations at various process steps. Our simulation results confirm qualitatively Voronkov's *v/G* theory, [2].

2 Multiscale model

The different length and time scales in Czochralski (CZ) silicon crystal growth lead to a hierarchy in the developed model. Heat transfer and point defect transport are coupled only in one way. Point defect dynamics are highly depending on the temperature in the crystal, but because of the low intrinsic point defect concentrations they do not influence the heat transfer in the crystal, [3].

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2.1 Heat transfer

Heat transfer in a Czochralski furnace occurs by conduction, convection and radiation. The equations for the temperature are

$$\rho_{0i} c_{pi} \left(\frac{\partial T_i}{\partial t} + u_i \cdot \nabla T_i \right) - \nabla \cdot (k_i \nabla T_i) = \rho_{0i} P_i$$

where ρ_{0i} is the density of the component, c_{pi} is the heat capacity, u_i is the velocity, k_i is the thermal conductivity and P_i is a heat source term. The index i indicates the different components of the apparatus, like melt, crystal, crucible, heaters, heat shields and insulators. The heat sources P_i are nonzero only in the heaters.

Convection in the melt is governed by the Navier-Stokes equation

$$\frac{\partial u_m}{\partial t} + (u_m \cdot \nabla) u_m - \upsilon \Delta u_m + \nabla p = \beta (T_m - T_0) g$$

$$\nabla \cdot u_m = 0$$

with u_m velocity, p pressure and T_m temperature, where the melt is Newtonian and variations of melt density are negligible, except in the calculation of the body force induced by thermal buoyancy, which is the onset of Grashof convection.

The influence of the gas flow is neglected. Further it is assumed that no radiation is emitted or absorbed by the gas and that radiation is only diffuse. Moreover, it is considered that emission, absorption and reflection of radiating waves occur only at the surfaces. The heat balance at the surface relating the heat flux caused by conduction to the surface q, the radiosity and the irradiation then becomes $q = G(\sigma T^4)$, with $G = (I - \varepsilon K (I - (1 - \varepsilon) K)^{-1})\varepsilon$. σ is the Stefan-Boltzmann constant, ε is the emissivity, the operator K is defined as

$$K\lambda(r) = \int_{\Gamma} \omega(r,s) \Xi(r,s) \lambda(s) ds, \forall r \in \Gamma$$

where $\Xi(r,s)$ is a visibility factor.

Along the free melt-crystal interface mass conservation and a no-slip boundary condition are valid. Due to the rotation of the crystal this no-slip condition is the onset of forced convection by crystal rotation. At the melt-crystal interface two thermal conditions have to be specified, $T_m = T_c = T_{eq}$ is set, where T_{eq} is the equilibrium melting temperature. The second thermal condition takes account of the heat flux balance between the two phases, the heat flux in the crystal is greater than in the melt by the amount of latent heat released during solidification, i.e. $k_m \nabla T_m \cdot \mathbf{n} - k_c \nabla T_c \cdot \mathbf{n} = \rho_{0c}\, l\, (\mathbf{u}_c - \mathbf{u}_f) \cdot \mathbf{n}$, with l the latent heat, $\mathbf{n}$ the normal vector and $\mathbf{u}_{\mathrm{f}}$ the speed of the phase-boundary.

The meniscus separating the melt from the ambient gas is another free interface, whose shape is part of the problem unknowns. Here again a Boussinesq-type approximation is made, where it is assumed that the surface-tension coefficient γ equals a constant γ_0, except in the boundary condition for the tangential stress. The temperature differences at the interface have an influence on the transport of momentum and heat near the interface. The surface-tension gradient resulting from this differences acts like a shear stress on the melt-gas interface and thereby generates a surface flow. This phenomenon is known as Marangoni convection.

It is assumed that the melt perfectly adheres to the crucible wall. A no-slip condition for the velocity is set at the crucible wall. This is the onset of forced convection due to rotation of the crucible. At the remaining boundaries only conditions for the temperature have to be set. At the surfaces of the melt, the crystal, the crucible, the heaters, heat-shields, insulators and the inner surface of the enclosure $k_i \nabla T_i \cdot \mathbf{n} = - \mathbf{G}(\sigma T_i^4)$ is taken, where i stands for the different components.

Initial conditions for the temperature T_i in all components of the apparatus, conditions for the velocity $\mathbf{u}_m$ in the melt and an initial domain for melt and crystal have to be described.

2.2 Point-defect dynamics

Point defects are incorporated into the crystal in their equilibrium concentrations and than diffuse and recombine rapidly in the high temperature portion of the crystal. In the model convection, Fickian and thermodiffusion and reaction of point defects in the growing crystal are considered. Fickian diffusion is driven by concentration gradients in the crystal, thermal diffusion is driven by temperature gradients in the direction of increasing temperature. Recombination is characterized by the annihilation of interstitials and vacancies and the creation of an undisturbed lattice site. The governing equations for the concentrations of interstitials and vacancies are

$$\frac{\partial C_i}{\partial t} + u_c \cdot \nabla C_i - \nabla \cdot (D_i \nabla C_i - \frac{Q_i D_i C_i}{k T_c^2} \nabla T_c) = k_{rec} (C_i^{eq} C_v^{eq} - C_i C_v)$$

$$\frac{\partial C_v}{\partial t} + u_c \cdot \nabla C_v - \nabla \cdot (D_v \nabla C_v - \frac{Q_v D_v C_v}{k T_c^2} \nabla T_c) = k_{rec} (C_i^{eq} C_v^{eq} - C_i C_v)$$

where C_i and C_v are the concentrations of interstitials and vacancies, D_i and D_v the temperature-dependent diffusion coefficients, Q_i and Q_v the activation enthalpy for thermal diffusion, C_i^{eq} and C_v^{eq} the equilibrium concentrations, k the Boltzmann constant and k_{rec} the reaction coefficient for recombination. Clustering of point defects is not taken into account because the point defect concentrations already reflect the latter grown-in defect distribution.

Dirichlet conditions with the equilibrium concentration are specified as boundary conditions along all crystal surfaces.

3 Numerical methods

Coupled heat transfer and point defect equations are solved by finite elements. The discretisation is based on the work in [4], [1] and [5]. For the melt, the heat conduction equation has been solved by adjusting an effective heat transport coefficient inside the melt, which has been extracted from temperature measurements and melt flow calculations, [6] and [7]. By this treatment we can approximate the influence of the melt flow without explicitly calculating the melt convection, which would increase the computational effort dramatically, due to the turbulent behaviour of the melt. With the existing computing power it is today not possible to solve a global heat transfer model for the whole growth process, where turbulent melt flow is included. But as long as impurity transport is not a major concern, neglecting the melt flow can already reproduce experimental measurements in a satisfactory way [8]. The integral equation to model heat radiation is discretized by piecewise constant elements. The method of [4] and [9] is used to calculate the view factors in rotational symmetric domains.

In most heat transfer simulation of Czochralski crystal growth processes, quasi steady state conditions are assumed. Transient simulations where geometry changes due to the growing of the crystal are taken into account where previously performed by [10], [11] and [12].

For the simulation of point defects, the influence of thermal diffusion is neglected in the numerical procedure. A parameter set for diffusivities and equilibrium concentrations obtained by [3] is used for the calculation which describes grown-in defect distributions for a large number of crystals grown under steady state process conditions for various hot zones and crystal diameters, [1]. Due to different time scales for temperature and geometry changes and point defect dynamics, a coupling between this phenomena is not necessary in each time step. Point defect concentrations evolve much faster than temperature changes in the crystal, therefore several time steps in the calculation of point defect concentrations are solved before the temperature and the crystal shape is updated. In previous transient point defect simulations [13], the growing of the crystal and the temperature change during the growing process were not taken into account.

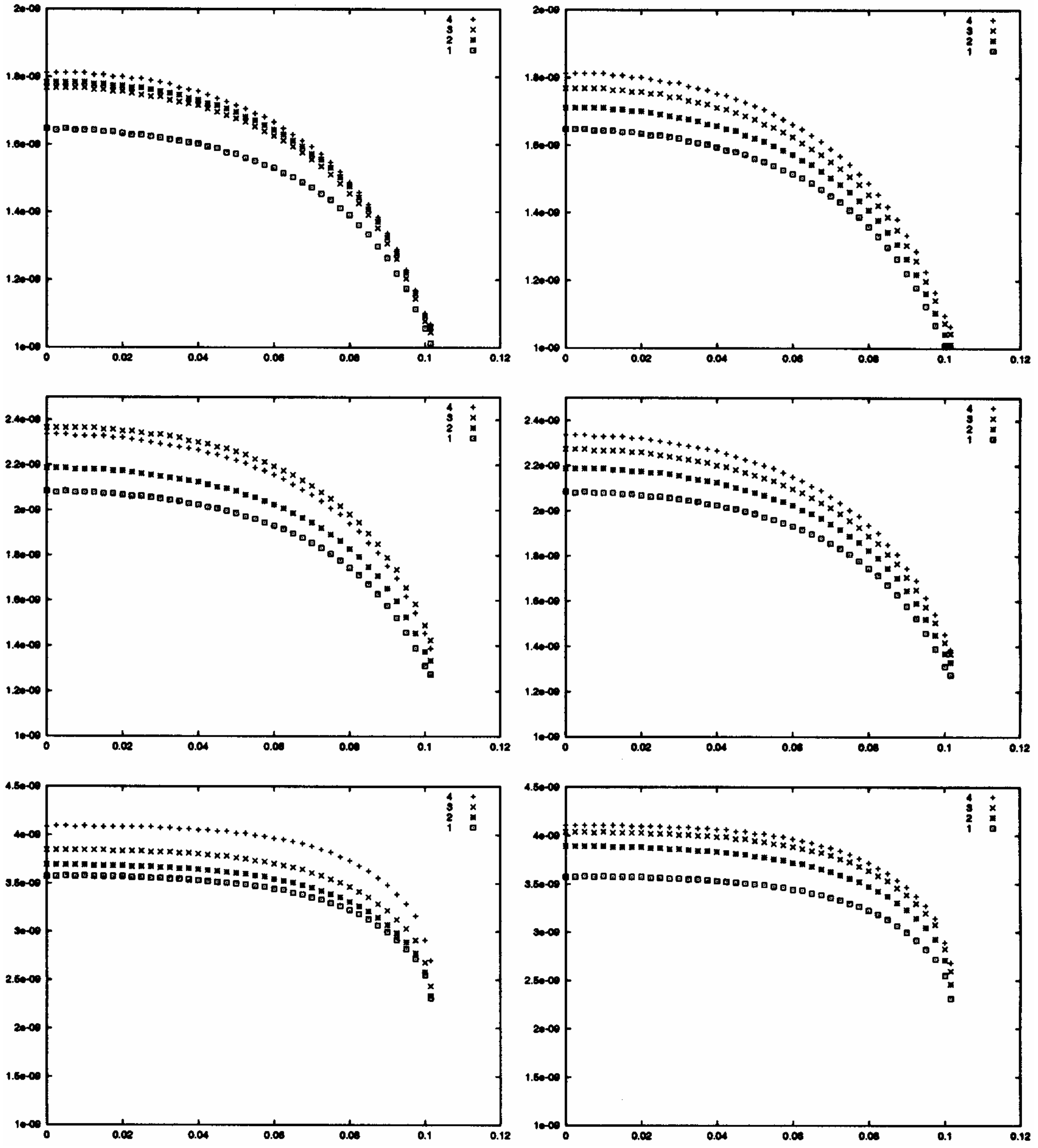

Fig. 1 v/G curve for pulling velocities v_{p1}, $v_{p2,}$ v_{p3} (from up to down) for quasi static and transient simulations (from left to right) at time steps 1 = 0 min, 2 = 85 min, 3 = 170 min and 4 = 250 min, v/G is measured in m^2/K s.

4 Results and discussion

The simulations are performed for an experimental furnace to grow crystals with 200mm diameter. In the same hot zone three different pull rates where used, v_{p1} = 0,348 mm/min, v_{p2} = 0,454 mm/min and v_{p3} = 0,892 mm/min, to simulate the growing process over a time interval of 250 min. All simulations start with an initial quasi steady state computation for a crystal length of 10 cm. Under the same settings quasi steady state simulations are performed at time steps, t_0 = 0 min, t_1 = 85 min, t_2 = 170 min and t_3 = 250 min. The aim of the simulation is the comparison of transient and quasi steady state simulations under constant growth conditions.

4.1 Temperature distribution

The computed temperature distributions in the crystal agree well with our experience from temperature measurements, [6]. The temperature profiles as well as the phase boundaries for transient and quasi steady state simulations show the same qualitative behaviour.

The upper part of the crystal continuously cools down during the growth process. The axial temperature gradient is larger close to the phase boundary and decreases with increasing crystal length. This qualitative behaviour is the same in both transient and quasi static simulations. Quantitative differences in the crystal are less than 5 K.

The calculations clearly show that the shape of the phase boundary depends on the crystal length. Under the same growth conditions, the phase boundary is more deflected for longer crystals. This is due to higher temperatures inside the crystal resulting from a lower surface to volume ratio for longer crystals which reduces the release of latent heat at the surface. This behaviour is the same for transient and quasi static simulations. The deflection of the phase boundaries differ by less than 1 mm.

The qualitative properties of the temperature profile and the shape of the phase boundary in quasi-static and transient simulations are identical. The maximal difference in the temperature value is less than 5 K, the difference in the deflection of the phase boundary is less than 1 mm. Quasi steady state assumptions in temperature simulations with reasonable constant pulling velocities are therefore good approximations of the time dependent growing process in order to describe the qualitative behaviour.

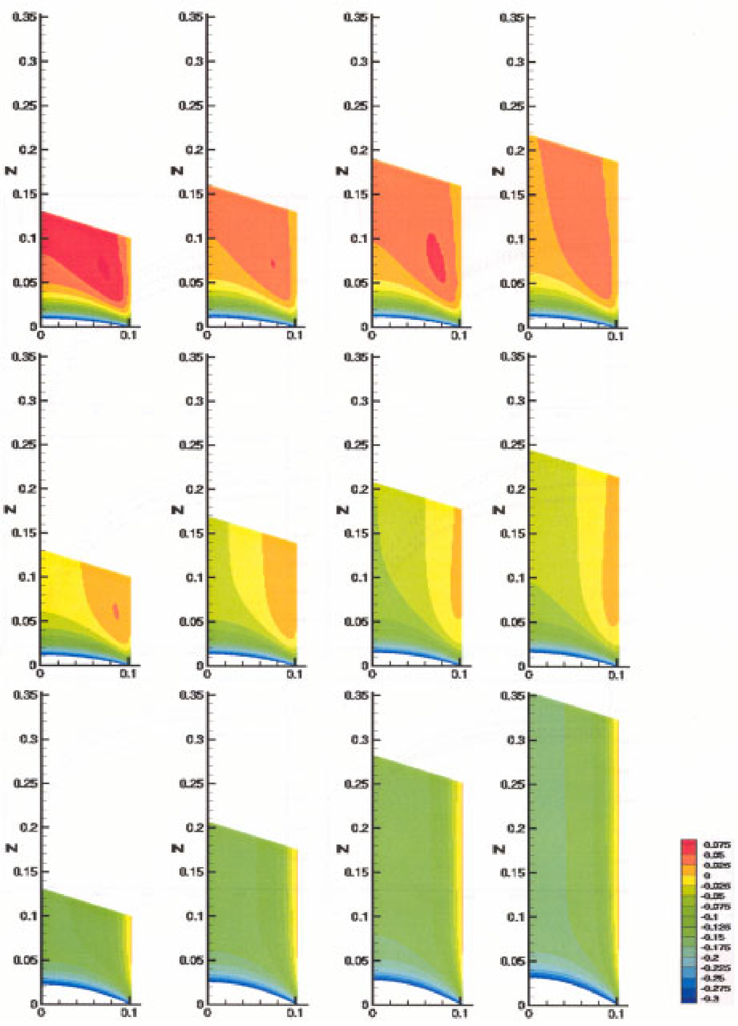

Fig. 2 Defect concentration for pulling velocities v_{p1}, v_{p2}, v_{p3} (from up to down) at time steps 1 = 0 min, 2 = 85 min, 3 = 170 min and 4 = 250 min (from left to right) for quasi-static simulations, a normed difference between C_i and C_v.

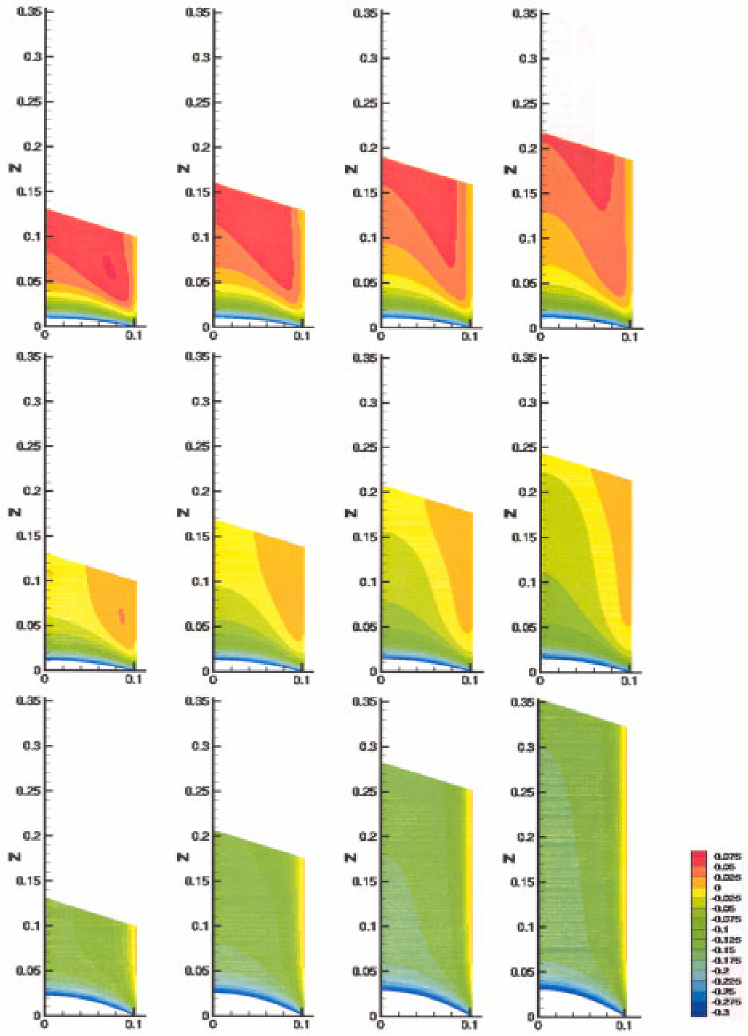

Fig. 3 Defect concentration for pulling velocities v_{p1}, $v_{p2,}$ v_{p3} (from up to down) at time steps 1 = 0 min, 2 = 85 min, 3 = 170 min and 4 = 250 min (from left to right) for transient simulations, a normed difference between C_i and C_v.

4.2 *v/G* curve

The temperature gradients at the growth interface play a crucial role in the study of intrinsic point defect distributions. The *v/G* curves for transient and quasi steady state simulations almost coincide (Fig. 1). The measured differences were less than 0.01 mm^2/K min. The decrease observed from centre to rim is due to high radiative heat loss. The decrease is higher for smaller crystals due to the higher surface to volume ratio. For v_{p1} *v/G* is below the critical value of 2.23 e-09 m^2/K s, [1], for v_{p2} *v/G* intersects the critical value and for v_{p3} *v/G* is above the critical value.

The *v/G* curve changes it's behaviour during time. This results from different temperature gradients at the solidification front. The curve for larger crystals lies always above the starting curve. This behavior is the same in transient and quasi static simulations. In order to describe qualitatively the point defect structure by *v/G*, quasi static simulations at various time steps should be performed. For reasonable constant pulling velocities they give good approximations of the time dependent behaviour of the *v/G* curve.

4.3 Point defect distributions

At the interface, interstitials and vacancies are incorporated at their equilibrium concentration of 1.0 e-15 and 1.2 e-15 cm^{-3}, respectively. Fast recombination in the high temperature part of the crystal reduces both concentrations. At a temperature of approximately 1200 K, axial point defect concentrations become stable.

Fully coupled transient heat and transient point defect simulations are performed. Highest interstitial concentrations occur in the crystal which is grown with the lowest pull rate v_{p1}. This crystal is fully interstitial-rich after cooling down. The crystal grown with pull rate v_{p2} shows vacancy-rich as well as interstitial-rich regions and the crystal grown with pull rate v_{p3} is completely vacancy-rich after cooling down. Fig. 2 and 3 show normalized differences between the concentration of interstitials and vacancies. Positive (red) values indicate an excess of interstitials, negative (blue) values an excess of vacancies. Qualitatively both quasi static and transient simulations predict the same defect species in the crystal. Comparing the results in Fig. 1 and 2 and 3 confirms Voronkow's qualitative v/G theory.

Quantitative differences on the other side can no longer be neglected. The transient results clearly show the dependency of the defect structure on the time evolution. Especially for v_{p2} the change between vacancy-rich regions in the centre and interstitial-rich regions on the outer part, the zero isoline, shows a different behaviour. The axial boundary between both regions in the quasi steady result indicates a stabilized situation assuming constant thermal situations during the whole growth process, where the transient results show an axial variation taking into account the different thermal conditions at various time steps. In order to not only estimate the defect species remaining in excess in the crystal but also indicate the concentration of the defects, time dependent simulations should be used, even for constant pulling rates.

5 Summary and conclusions

Coupled transient heat transfer and transient point defect transport have been successfully simulated with constant pull rates for growing silicon crystals. The simulation results coincide qualitatively with quasi steady state simulations for heat transfer. This results show that for constant pull rates transient simulations are not necessary in order to calculate the temperature distribution in the crystal.

This simplification is probably not true if strong transient effects like changing the pulling speed or temporary halting the growth are applied. This phenomena will be addressed in a forthcoming paper.

Already for constant pulling velocities the simulation results show a dependence of the shape of the phase boundary on the crystal length. Qualitative statements about the intrinsic point defect distribution are possible with quasi steady simulations for temperature and defects. But the change in the phase boundary during the growth process influences the defect distribution. In order to predict the concentration of intrinsic point defect in the crystal the thermal history of the crystal should therefore no longer be neglected.

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